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(54) Fluorocarbon ethers having substituted halogen site(s) and process to prepare.

(57) Novel perhalofluoro ethers and methods for preparing the same having generic formula,

$$Y(CF_2)_a\text{-}(CFR_f)_b\text{-}CFR'_f\text{-}O\text{-}\left(\begin{matrix}CF\text{-}CF_2\text{-}O\\ |\\ CF_2X\end{matrix}\right)_n\begin{matrix}CF\text{-}C=O\\ |\\ CF_2X'\end{matrix}\quad \begin{matrix}|\\ Z\end{matrix}$$

wherein
a is 0 or an integer greater than 0;
b is 0 or an integer greater than 0;
m = zero or an integer greater than zero;
n = zero or an integer greater than zero;
R_f and R' are each independently selected from the group consisting of F, Cl, perfluoroalkyl and fluorochloroalkyl;
X = F, Cl, Br, or mixtures thereof when n>1;
X' is independently Cl or Br, or mixtures thereof;
Y is an acid group or an acid derivative easily convertible to an acid group;
Z = F, Cl, Br, OH, NRR' or OA;
R and R' are independently selected from the group consisting of hydrogen, an alkyl having one or more than one carbon atom and aryl;
A = alkali metal, quaternary nitrogen, or R.
These compounds may be reacted to form various derivatives.

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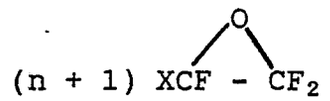
FLUOROCARBON ETHERS HAVING SUBSTITUTED HALOGEN SITE(S) AND PROCESS TO PREPARE

The present invention relates to a novel class of fluorine containing ethers and methods for their preparation.

U.S. Patent 3,301,893 teaches reacting



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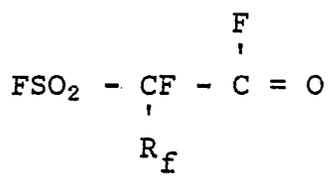
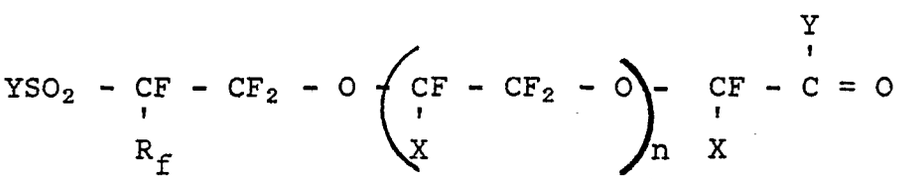


to form compounds represented by the general formula



where

R_f is F or perfluoroalkyl radicals having from 1 to 10 carbon atoms;

X is F or a trifluoromethyl radical, or mixtures thereof, where there is more than one X;

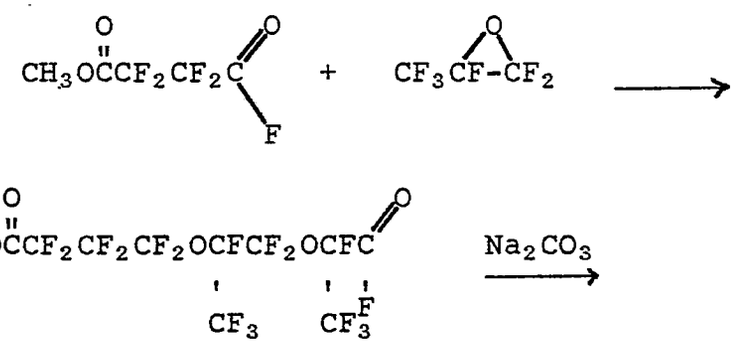
Y is a radical selected from the group consisting of fluorine, amino, hydroxyl and OMe radical where Me is a radical selected from the group consisting of the ammonium radical, alkali metals and other monovalent metals; and

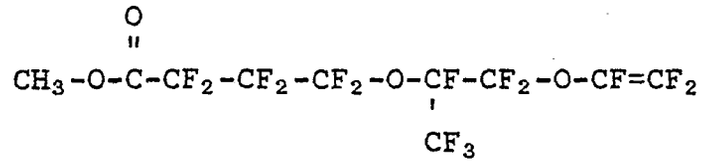
n is a number from 0 to 12.

U.S. Patent 3,536,733 teaches the preparation of compounds represented by the general formula

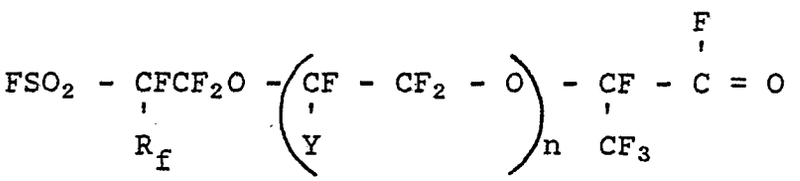
where Y is F or CF_3.

British patent 1,518,387 teaches the following reactions.

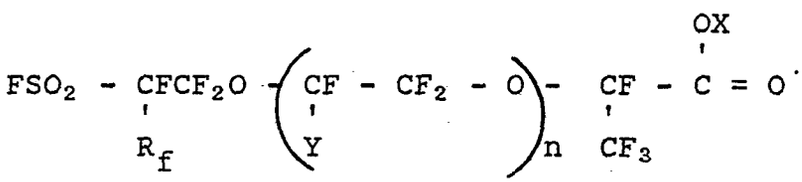




U.S. 3,282,875 teaches pyrolyzing compounds having the general formulas



and



to form compounds represented by the general formula

where

R_f is F or a perfluoroalkyl radical having from 1-10 carbon atoms;

Y is F or a trifluoromethyl radical;

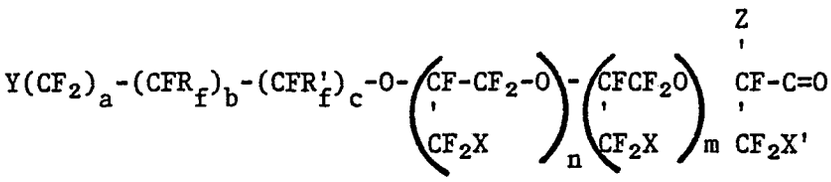
n is an integer of 1-3, inclusive;

M is F, hydroxyl radical, amino radical or OMe; and

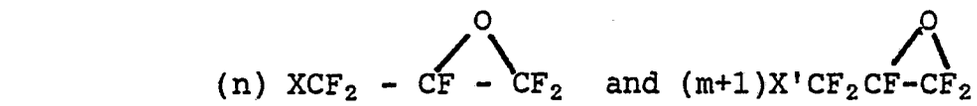
Me is an alkali metal or quaternary nitrogen radical.

X is alkali metal

The present invention resides in novel compounds represented by the general formula



and in the method of preparing the compounds by reacting



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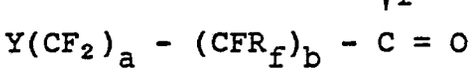


wherein a is 0 or an integer greater than 0;
b is 0 or an integer greater than 0;
c is 0 or 1 provided that a + b + c ≠ 0;
m = zero or an integer greater than zero;
n = zero or an integer greater than zero;
R'_f and R_f are independently selected from the group consisting of F, Cl, perfluoroalkyl and fluorochloroalkyl radical;
X = F, Cl, Br, or mixtures thereof when n>1;
X' is independently Cl, Br, or mixtures thereof;
Y is an acid group or an acid derivative easily convertible to an acid group;
Z = F, Cl, Br, OH, NRR' or OA;
R and R' are independently selected from the group consisting of hydrogen, an alkyl having one or more than one carbon atom, and an aryl;
A = alkali metal, quaternary nitrogen, or R.

Preferably, when R_f'; R_f; R, and R' are alkyl or aryl radicals, they have from 1 to 10, more preferably from 1 to 4 carbon atoms.

Preferably, Y may be SO_2-Z, $\overset{Z}{\underset{|}{C}}$=O, $\overset{|}{P}$=O or $C\equiv N$ or $\underset{(Z)_2}{\overset{|}{}}$ other appropriate groups (as Z is defined above).

The compounds of the invention are intermediates which may be further reacted to form a novel class of monomers, which, in turn, may then be polymerized and used in the preparation of chemically stable ion exchange resins or membranes.

When the polymers ultimately derived from the intermediates of the invention are formed into sheets for use as membranes such as in chlor-alkali cells, it is desirable to choose Z so that the polymers formed are thermoplastic to allow fabrication by conventional means, such as melt extrusion. After fabrication they can be easily converted to the acid or alkali metal salt of the acid. As an example, when Y = SO_2F (Z=F), the intermediate is converted to an olefin monomer still having the $-SO_2F$ group. The monomer is then copolymerized to form a polymer containing the SO_2F group that can be formed into sheets by various plastic fabrication techniques. After fabrication, the SO_2F group is easily converted to the alkali metal salt of the corresponding sulfonic acid, $-SO_2ONa$ (Z= ONa), which can be converted to the sulfonic acid, $-SO_2OH$ (Z= OH), by reaction with acids, such as mineral acids.

$$-SO_2F + NaOH \longrightarrow -SO_2ONa + NaF \xrightarrow{HCl} - SO_2OH + NaCl$$

When Y is chosen as $-C\equiv N$, a nitrile, the above conditions are met since it is well known that nitriles are converted to carboxylic acids by hydrolysis.

When the polymers derived from the olefins from the present intermediates are to be used in particle or powder form, such as for acid catalyst, it is not critical in the choice of Z since fabrication is not as large a factor. In this case, Z can conveniently be any of the radicals listed. It can be -OH so as to directly have Y as an acid group or it can be any group rendering Y convertable to an acid group by further reaction.

X is chosen from the halogens Cl, Br or F, while X' is chosen from Cl or Br. While iodine would also be useful for X or X', formation of the ethers by the chemistry taught herein is hampered by side reactions causing low or nonexistant yields to the desired compounds.

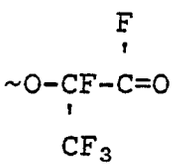
When X' = Cl or Br and X = F, Cl or Br, new uses and novel and surprising new chemistry results from using the intermediates for additional chemical reactions. The prior art teaches that when Y = SO_2F, n = 0, M=O, and X' = F (U.S. Patent No. 3,560,568) reaction of the intermediate with a base does not produce the desired vinyl ether monomer, but rather a cyclic sulfone compound. Surprisingly, when n = 0, M = O, Y = SO_2F and X' = Cl or Br, reaction of the intermediate with a base produces the desired vinyl ether product in one step. In addition to this benefit, choosing X or X' = Cl or Br in compounds where m or n > 0 results in introducing a potential reaction site into polymers ultimately derived from monomers made from these intermediates. When m or n > 0 both an acid site for ion exchange or catalyst (Y) and a reaction site for further reaction can be obtained by having X or X' = Cl

or Br. In general, metallation reagents such as alkyl alkali metals can be used for reactions on these reaction sites.

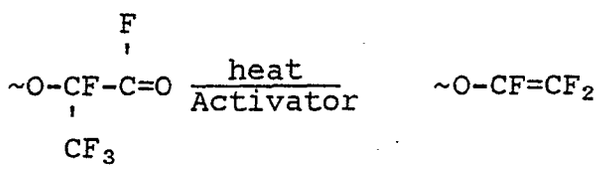
There is an additional benefit for having X' = Cl or Br. In this case it is helpful to have Cl or Br in this position for the subsequent reactions and uses for these compounds.

The variables in the structures have preferred values as follows: n = 0 - 6, m = 0 - 6, a = 0 - 3, b = 0 - 3. Preferred is n = 0 - 3 and m = 0 - 3. Most preferably n = 0 or 1 and m = 0 or 1. Preferably X = Cl, X' = Cl and Y = $Z'SO_2$. More preferably Y = $Z'SO_2$ and Z' = F. R_f and R_f' are preferably F.

In decarboxylations of the prior art, compounds of the terminal functionality shown below are common.



These materials generally require high temperatures and activators such as ZnO or silica to achieve reasonable yields to the desired vinyl ethers.



When X' is Cl or Br in the present invention, decarboxylation of these intermediates to vinyl ethers has been found to proceed under mild conditions and in excellent yields.

The novel class of compounds of the present invention are conveniently prepared by reacting an acylfluoride or ketone of the general formula

$$Y(CF_2)_a - (CFR_f)_b - \overset{R'_f}{\underset{|}{C}} = O$$

with perhalofluoro propylene epoxide of the formulas

$$XCF_2 - \underset{\diagdown\,O\,\diagup}{CF} - CF_2 \quad \text{and} \quad X'CF_2\underset{\diagdown\,O\,\diagup}{CF}-CF_2$$

where Y, R_f, R'_f, a, b, X' and X are as defined above. The reactions are done in the presence of a fluoride ion yielding compound metal fluoride-catalyst (MF) at a temperature and a time sufficient to cause a reaction, preferably from -20°C to 50°C, in the liquid state, desirably in a liquid solvent for the intermediate fluoroalkoxide $Y(CF_2)_a - (CFR_f)_b - CFR'_fO^-M^+$ formed between the acid fluoride or ketone

$$Y(CF_2)_a - (CFR_f)_b - \overset{R'_f}{\underset{|}{C}} = O.$$

and the metal or ammonium fluoride, fluorine ion yielding catalyst (MF). The reactions proceed generally according to the equation

$$(n)XCF_2-\underset{\diagdown\,O\,\diagup}{CF}-CF_2 \quad + \quad Y(CF_2)_a-(CFR_f)_b-\overset{R'_f}{\underset{|}{C}}=O \xrightarrow{MF}$$

$$Y(CF_2)_a - (CFR_f)_b - CFR'_f - O - \left(\begin{matrix} CF - CF_2 - O \\ | \\ CF_2X \end{matrix}\right)_n - \begin{matrix} CF - C = O \\ | \\ CF_2X \end{matrix}$$

These acid fluoride intermediates can then be reacted with (m+1) $X'CF_2\overset{O}{\overset{/\backslash}{CF-CF_2}}$ to produce ethers having the general formula

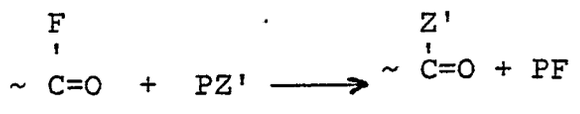
$$Y(CF_2)_a(CFR_f)_b(CFR'_f)_cO-\left(\begin{matrix} CFCF_2O \\ | \\ CF_2X \end{matrix}\right)_{n+1}\left(\begin{matrix} CFCF_2O \\ | \\ CF_2X' \end{matrix}\right)_m \begin{matrix} CFC=O \\ | \\ CF_2X' \end{matrix}$$

The latter reaction is preferable when X=F, and the intermediate is to be decarboxylated to a vinyl ether. When X=X'=Cl, Br, only the first reaction is necessary to form the desired compounds.

wherein a is 0 or integer greater than 0;
b is 0 or integer greater than 0;
c is 0 or 1 provided that a + b + c ≠ 0;
m = zero or an integer greater than zero;
n = zero or an integer greater than zero;
R'_f and R_f are independently selected from the group consisting of F, Cl, perfluoroalkyl and fluorochloroalkyl;
X = F, Cl or Br;
X' = Cl or Br;
Y is an acid group or an acid derivative easily convertible to an acid group;

Conversion of acid halides such as the acid fluorides described herein to carboxylic acids and

derivatives by reaction with nucleophiles is well known to those skilled in the art. For example, conversion of the acid fluoride to the corresponding carboxylic acid is easily accomplished by reaction with water. Conversion to esters or amides is accomplished by reaction with alcohols or amines, respectively. The carboxylic acids (Z = OH) are easily converted to acid chlorides or bromides (Z = Cl, Br) by reaction with appropriate halogenation agents such as PCl_5 or PBr_5. Reactions of the carboxylic acid fluoride proceed according to the following equation:



where

Z' = OH, NRR' or OR;

R and R' are independently selected from the group consisting of hydrogen, an alkyl having one or more than one carbon atom and aryl;

P is a cation or capable of forming a cation, such as Na^+, K^+, H^+, etc.

It is of course to be understood that in the reaction of the acid fluorides or ketones with the epoxides the ratio of reactants, the temperature of reaction, the amount of catalyst, as well as the amount and kind of solvent, influence the course, speed and direction of the reaction. Naturally the ratio of reactants bears more directly on the value of m and n in the generic formula than the other factors noted. For example, employing 1 or more moles of acid halide compound per mole of perhalofluoro epoxide results in a

product rich in the n=0 product, i.e., greater than 1.5 n=0 to n=1, respectively and if the ratio is 2 to 1, respectively, the n=0 product, respectively, is about 92 to 1, respectively, whereas employing greater than 1 mole epoxide compound per mole of acid fluoride compound, i.e., 2 to 1, respectively, results in a product having a 3:9:1 ratio of n=2: n=1:n=0 products. The ratio of reactants thus can range, for practical purposes, from about 2 to 3 moles of the acylfluoride or ketone per mole of the halofluoro epoxide to 1 to 20 moles of the epoxide per mole of the acyl fluoride, the high acyl fluoride to epoxide producing predominantly the n=0 and the high epoxide to acyl fluoride producing the n=2-12 ether, respectively, and mixtures thereof.

Solvents employed in accordance with the present invention should be non-reactive (e.g., do not contain hydroxyl groups) and have at least a solubility for the reactants and the intermediate fluoroalkoxide formed between the acyl fluoride or ketone compound and the catalyst. Whether or not the products are significantly soluble in the solvent is a matter of choice and can be used as a controlling factor for selectively controlling the n value in the final product. For example, if a high n value is desired, it is advantageous that the product having at least n=0 to 1 be soluble in the solvent to give the intermediates (n=0 and n=1) time to react to produce the final n=1, 2 or higher product. In addition, the amount of solvent can be adjusted to accomplish somewhat similar results. Generally, when the ratio of the weight of solvent to the weight of the acid fluoride is from about 0.3:1 to about 0.8:1, formation of the n=0 product is maximized. As the weight ratio increases, higher n values are

obtained. Although there is no theoretical maximum amount of solvent which may be used, one may quickly determine the weight ratio to be used depending upon the value of the n that he desires. Suitable solvents which may be employed to take advantage of the solubility plus amount factor are, for example, tetraglyme, diglyme, glyme, acetonitrile, or nitrobenzene. Exemplary of a preferred solvent is tetraglyme which has a suitable solvency for the intermediate, but in a weight to weight ratio has limited solubility for the product n=0 and therefore can be used advantageously to precipitate the n=0 product (remove it from the reaction media), effectively controlling (minimizing) the production of higher n values, yet if higher n values are desired, greater quantities of the solvent can be employed to dissolve the product n=0 or an amount sufficient to maintain a quantity thereof in the reaction medium to permit the epoxide to further react with the n=0 product to produce higher n value products. By controlling the amount, again it is possible to salt-out the intermediate n-values as a function of their solubility and quantity in the solvent-reaction media.

In a somewhat similar manner, the catalyst amount functions as a control of the end product n value. While the source of the fluoride ion is not critical, the amount of catalyst will to a significant measure establish the reactivity of the acid fluoride and thus determine the rate of reaction of the acid fluoride with the epoxide. Significant amounts of the catalyst, up to stoichiometric amounts based on the acid fluoride or ketone, will favor epoxide reacting on the feed acid fluoride. Whereas lesser catalytic amounts, with respect to the acid fluoride will favor

the reaction of the epoxide with the n=0 acid fluoride product forming higher n products. As has been noted, substantially any fluoride ionizable at the reaction conditions may be used as a catalyst, however, CsF and KF are the most preferred but AgF, tetra alkyl ammonium fluoride as well as others listed by Evans, et al., J. Org. Chem. 33 1837 (1968) may be employed with satisfactory results.

The temperature of the reaction also effectuates a controlling factor on the end product obtained. For example, low temperatures such as -20°C favor n=0 products and higher temperatures, 50°C and above, favor higher n values.

In summary, the following table illustrates the effect each parameter of the reaction has on the n value of the final product.

	n = 0 ———	n = 12
Ratio of ketone or acyl fluoride to epoxide	3/1	1/20
Solvent amt.	small	large
Temp.	low	high
Catalyst	high	low

EXAMPLES

EXAMPLE 1

90 ml of dry tetraglyme and 39.5 gms of anhydrous CsF were added to a 500 ml 3-neck flask

equipped with a stirrer, thermometer, reflux condenser at a temperature of -78°C, and an inlet port. Downstream of the reactor were liquid N_2 cold traps maintained at a temperature of 78°C. A slight back pressure was maintained on the system with dry N_2.

The reactor was cooled to 0°C to 5°C and 126 grams of fluorosulfonyldifluoroacetylfluoride

$$FSO_2 - CF_2 - \underset{\underset{F}{|}}{C} = O,$$

were added slowly over a 20 minute period and then allowed to mix for another 20-30 minutes to ensure formation of the alkoxide.

64.3 grams of $ClCF_2 - \underset{\diagdown\,O\,\diagup}{CF} - CF_2$ were added slowly over an hour and 45 minutes while maintaining the reactor temperature at 0° to 5°C. After the epoxide addition, the contents were allowed to mix for an additional hour. The temperature was allowed to rise to room temperature. When stirring ceased, two separate layers formed. The bottom layer was drawn off and weighed 104.7 grams. VPC (Vapor Phase Chromatography) analysis of this product showed 92% n=O product and 7.85% lights or product formed by reaction of the epoxide with itself.

Conversion of the epoxide was essentially complete. Yield of epoxide to the n=O product was 75.3%.

The products were analyzed further by GC-MS (Gas Chromatography-Mass Spectrophotometry) and the following compounds were identified:

$$Cl(CF_2)_3 - O - \underset{\underset{CF_2Cl}{|}}{CF} - \underset{\underset{F}{|}}{C} = O$$

as the light material

$$FSO_2(CF_2)_2 - O - \underset{\underset{CF_2Cl}{|}}{CF} - \underset{\underset{F}{|}}{C} = O$$

as the n=0 product

Products were analyzed further by IR. The -COF groups present at 1870-1880 wave no., $-FSO_2$ group at 1460 and 1240 wave nos.; and -SF at 810 wave number for n=O product.

The products had retention times of 1.35 and 2.74 minutes, respectively, on a VPC using six feet columns of 20% Viton® on Celite®. Column temperature of 60°C.

EXAMPLE 2

35 ml of dry tetraglyme and 15.6 gms CsF were added to a 3-neck 100 ml flask equipped with a stirrer, thermometer, (-78°C) reflux condenser and an inlet port. Downstream of the reactor were two (-78°C) cold traps in series. A slight back pressure was maintained with dry N_2. Tetraglyme and CsF were mixed for 45 min. to 1 hour.

The reactor was cooled to 0°C to 5°C and 49.32 grams of fluorosulfonyl difluoro acetyl fluoride

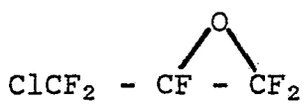
$$FSO_2 - CF_2 - \underset{\underset{F}{|}}{C} = O$$

were added slowly over a 20 minute period, allowed to mix at 0° to 5°C for 2 hours and then the temperature was raised slowly to room temperature to ensure the formation of the alkoxide. After cooling the reactor to 0°C, 25 grams of chloropentafluoropropylene oxide,

$ClCF_2 - CF - CF_2$, were added slowly over a 3-4 hour period. After the epoxide addition was complete, the contents were mixed for an additional hour. The temperature was allowed to rise to room temperature. When stirring was stopped, two liquid phases separated. 38.94 gms of the heavy or bottom layer was collected. Analyses by VPC showed 87.86% of n=0 product, 5% unreacted reactants, and 4.2% of a higher molecular wt. product. This gave an essentially complete conversion of the epoxide and a 68.9% yield of epoxide to the n=0 product.

The unreacted reactant (FSO_2CF_2CFO) was distilled off the product.

35 ml of tetraglyme and 8 gm CsF were mixed for 40 minutes. The heavies from the above distillation were added slowly over a 20 minute period and mixed for 1 hour at 0°C to 5°C. The reactor was warmed to room temperature to ensure formation of the alkoxide. After cooling again to 0°C to 5°C, 19.6 grams of

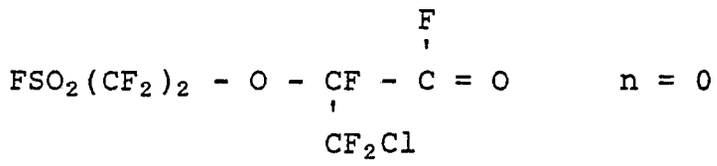


$ClCF_2 - CF - CF_2$

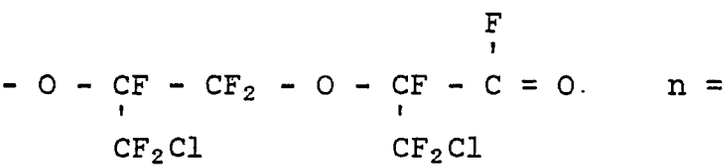
were added slowly over a 2-3 hour period, and then allowed to mix at 0°C to 5°C for another hour. The reactor was warmed to room temperature. After stirring was stopped, two separate layers formed. 35.67 grams

of bottom or product layer was collected. Analyses by VPC showed 12.8% n=0 product, 57.4% n=1, and 6.8% n=2 product. Thus, of the n = o product that reacted, 45.9% was converted to the n=1 product.

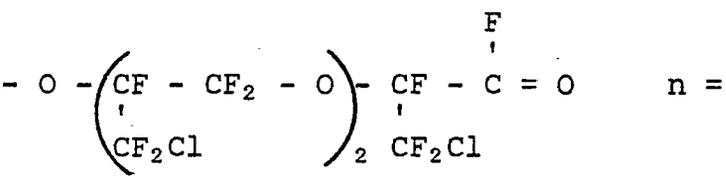
The following products were identified by mass spectrometer:



$$FSO_2(CF_2)_2 - O - \underset{\underset{CF_2Cl}{|}}{CF} - \underset{\underset{F}{|}}{C} = O \qquad n = 0$$



$$FSO_2 - (CF_2)_2 - O - \underset{\underset{CF_2Cl}{|}}{CF} - CF_2 - O - \underset{\underset{CF_2Cl}{|}}{CF} - \underset{\underset{F}{|}}{C} = O \qquad n = 1$$



$$FSO_2 - (CF_2)_2 - O - \left(\underset{\underset{CF_2Cl}{|}}{CF} - CF_2 - O\right)_2 - \underset{\underset{CF_2Cl}{|}}{CF} - \underset{\underset{F}{|}}{C} = O \qquad n = 2$$

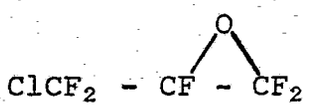
Mass spectroscopy fragmentation pattern reported consistent with this structure of n=2.

The infrared showed the characteristic SO_2F and $-C\overset{O}{\underset{F}{}}$ bands, VPC retention times using the column described in Example 1 with a temperature program of 4 min. at 60°C, followed by a rise to 220°C at 16°/min. were 2.72, 5.74, and 8.18 minutes, respectively.

EXAMPLE 3

75gm of $FSO_2(CF_2)_2 - O - \underset{\underset{CF_2Cl}{|}}{CF} - \overset{\overset{F}{|}}{C} = O$

was added dropwise to a 500 ml vessel containing 200 gm tetraglyme and 15.2 gm CsF. The vessel was fitted with a cold finger condenser and two traps on the effluent; one dry ice acetone and the other liquid nitrogen. The acid fluoride was stirred for one hour after the addition was completed and then



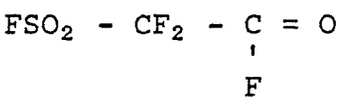
was added at a rate such that no reflux was observed on the cold finger. A total of 18.3 gm was added, keeping the temperature below 35°C. After completing the addition, the mixture was stirred for an hour. The vessel contents were poured into a separatory funnel under dry nitrogen blanket and the lower product layer was allowed to settle out. The product layer was drained off and analyzed chromatographically as: 1 part n=3, 1.1 parts n=2, 12 parts n=1, 4.6 parts residual n=O.

EXAMPLE 4

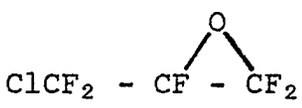
30 ml of dry tetraglyme and 14.15 gms (.0932 mole) CsF were added to a 100 ml 3-neck flask equipped with a stirrer, thermometer, (-78°C) reflux condenser, and an inlet port. Downstream of the reactor were two (-78°C) cold traps in series. A slight back pressure was

maintained on the system with dry N_2. Tetraglyme and CsF were mixed for at least 45 minutes.

The reactor was cooled to -20°C and 16.83 gm (.093 moles) of

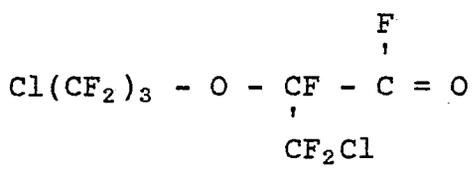


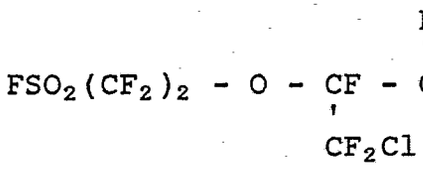
added. The temperature was brought up to 20-25°C and 30.2 gm of

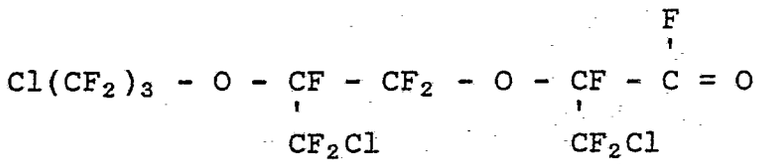


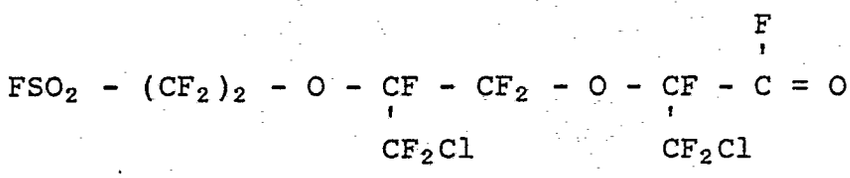
were added in increments of 2 to 3 grams over a 4 hour period while maintaining the reactor at 25-28°C. After the epoxide addition, the contents were stirred for an additional 1.5 hours. When stirring ceased, two separate layers formed and were separated with a separatory funnel. 28 gm of product (bottom layer) were collected. Analysis by VPC showed 13.4% n=0 product, 33.8% n=1 product, and 4.3% n=2 product. In addition, there were products (dimers and trimers) of the epoxide.

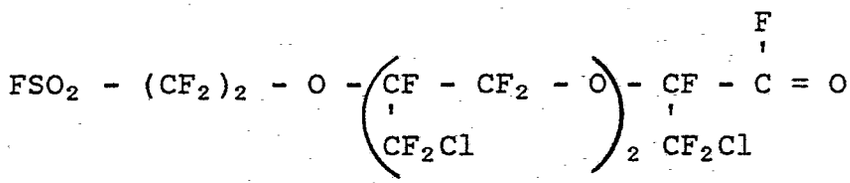
Products were analyzed further by GC-MS and the following compounds were identified:





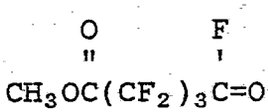




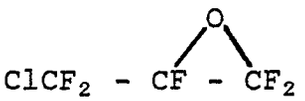


EXAMPLE 5

200 ml of dry tetraglyme and 15.19 gms (0.10 moles) of CsF were added to a 500 ml 3-neck flask equipped with a stirrer, thermometer, (-78°C) reflux condenser, and an inlet port. Two (-78°C) cold traps in series were located downstream of the reflux condenser. A slight back pressure was maintained on the system with dry N_2. After stirring for 1 hour, the reactor was cooled to -5°C, and 51.22 gms (0.20 moles) of methyl perfluoroglutaryl fluoride



were added dropwise. The reactants in the reactor were stirred overnight at room temperature. Reactor was cooled to -5°C and 18.25 gms (0.10 moles) of chloropentafluoro propylene oxide

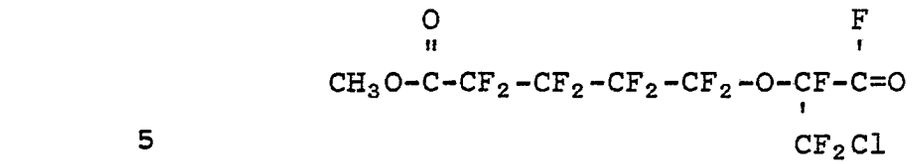


were added slowly. After the epoxide addition was complete, samples were taken after 30 min. and 1.5 hr. and analyzed by VPC. The temperature was then raised to room temperature over one hour period and sample analyzed by VPC.

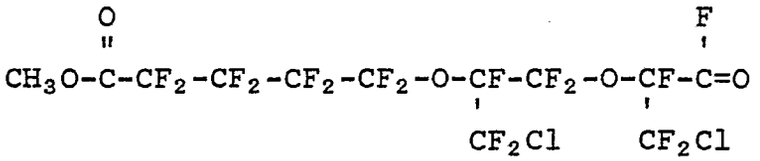
The products were distilled out of the reactor under 30" vacuum while heating to 160°C. The overhead temperature was 65°C at this point. 49.38 gm of the product was collected in the first cold trap and 2.5 gms was collected in the second trap. The products were analyzed by VPC.

The material caught in the first cold trap was distilled in a microcolumn to remove the unreacted methylperfluoroglutaryl fluoride. All material boiling up to 145°C was removed in this manner. Everything heavier was retained in the pot and weighed 18.44 grams. Heavies were analyzed by VPC, mass spectroscopy and I.R. (Infra Red).

Peaks on the VPC were 7.21, 7.62, 8.86, and 10.47 minutes. Mass spectroscopy showed that the 7.21 peak had the structure



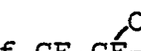
the 8.86 peak had the structure



IR analysis showed bands at 2960, 1860, and 1770-1780 Cm^{-1}. The 1860 Cm^{-1} band is the -COF group and

the 1770-1780 Cm^{-1} is the ester -C- group. The 2960 Cm^{-1} is due to the CH_3 group.

Example 6

25 ml of tetraglyme and 6.9 gms of CsF were added to a 50 ml, 3 neck flask equipped with a stirring bar, thermometer, reflux condenser, and an inlet port. Two (-78°C) cold traps in series were located downstream of the reflux condenser. A slight backpressure was maintained on the system with dry N_2. The tetraglyme and CsF were allowed to mix for 1 hour at room temperature, lowered to 10°C-20°C, and 48 grams of FSO_2CF_2CFO were added and allowed to mix for 1 hour. The mixture was cooled to 0°C and 25 grams of  were added over an hour and 20 minute period, while maintaining a temperature of 0°C to 10°C. After mixing at this temperature for 2 hours, the temperature was increased to room temperature. The product was separated as a clear, dense, bottom layer. 50.5 grams were recovered which was determined to be 80.16%

$$FSO_2CF_2CF_2O\underset{CF_3}{\underset{|}{C}F}CFO$$

by VPC analysis.

The lower boiling components were removed leaving a mixture containing 88.6% of the desired acid fluoride.

5 ml of tetraglyme and 1.7 gms CsF were added to a 50 ml 3 neck flask equipped as above and the mixture was stirred for 30 minutes. 5 grams of distilled $FSO_2CF_2CF_2O\underset{CF_3}{\underset{|}{C}F}CFO$ were added and mixed at 10°-20°C for 1 hour. 1.4 gms of $ClCF_2\overbrace{CF-CF_2}^{O}$ were added while maintaining a temperature of 0° to 10°C, and held at this temperature for 1 hour. The temperature was increased to room temperature, 5 ml of tetraglyme added, and the product separated from the solvent. 3.0 grams of product were obtained and analyzed as 63.98%

$$FSO_2CF_2CF_2O\underset{CF_3}{\underset{|}{C}F}CF_2O\underset{CF_2Cl}{\underset{|}{C}F}CFO$$

having a 6.47 minute retention on the VPC and confirmed by I.R. and mass spectroscopy.

1. A composition represented by the general formula

$$Y(CF_2)_a - (CFR_f)_b - (CFR'_f)_c - O - \left(\begin{matrix} CF-CF_2-O \\ | \\ CF_2X \end{matrix}\right)_n - \left(\begin{matrix} CF-CF_2O \\ | \\ CF_2X' \end{matrix}\right)_m - \begin{matrix} Z \\ | \\ CF-C=O \\ | \\ CF_2X' \end{matrix}$$

where

a = 0 or an integer greater than 0;

b = 0 or an integer greater than 0;

c = 0 or 1 provided that a + b + c ≠ 0;

m = 0 or an integer greater than zero;

n = zero or an integer greater than zero;

R_f and R'_f are each independently selected from the group consisting of F, Cl, perfluoroalkyl and fluorochloroalkyl;

X = F, Cl, Br, or mixtures thereof when n > 1;

X' = Cl, Br, or mixtures thereof;

Y is an acid group or an acid derivative easily convertible to an acid group;

Z = F, Cl, Br, OH, NRR' or OA;

R and R' are independently selected from the group consisting of hydrogen, an alkyl having one or more carbon atom and aryl;

A = alkali metal, quaternary nitrogen, or R.

2. The compounds of Claim 1 where Y is selected from the group consisting of

$$Z'SO_2, \quad \underset{(Z')_2}{P=O}, \quad \underset{(Z')}{C=O} \text{ or } C\equiv N$$

where

Z' is F, Cl, Br, OH, NRR' or OA

R and R' are independently selected from the group consisting of hydrogen, an alkyl having one or more than one carbon atom and an aryl,

A is an alkali metal, quaternary nitrogen or R.

3. The compounds of Claim 1 or 2 wherein n = 0 - 6 and m = 0 - 6.

4. The compounds of Claim 1, 2 or 3 wherein X' = Cl.

5. The compounds of Claims 1, 2 or 3 wherein X = F and n is 1 to 4.

6. The compounds of Claims 1, 2 or 3 wherein X = F, X' = Cl and n is one and m is zero.

7. A method for preparing compounds of the formula

$$Y(CF_2)_a - (CFR_f)_b - (CFR'_f)_c - O - \left(\underset{CF_2X'}{CF} - CF_2 - O\right)_n - \underset{CF_2X'}{CF} - \overset{F}{C} = O$$

which comprises reacting compounds of the formula

$$X'CF_2 - CF\overset{O}{\diagdown\diagup} - CF_2$$

with compounds of the formula

$$Y(CF_2)_a - (CFR_f)_b - \underset{R'_f}{C} = O$$

for a time and a temperature sufficient to form said compound;

wherein

a = 0 or an integer greater than 0;

b = 0 or an integer greater than 0;

c = 0 or 1 provided a + b + c ≠ 0;

n = zero or an integer greater than zero;

R_f and R'_f are each independently selected from the group consisting of F, Cl, perfluoroalkyl and fluorochloroalkyl;

X' is independently Cl or Br;

Y is an acid group or an acid derivative easily convertible to an acid group;

8. The method of Claim 7 wherein n = 0 - 6, a = 0 - 3 and b = 0 - 3.

9. The method of Claim 7 or 8 wherein Y is selected from the group consisting of

$$Z'SO_2, \quad \underset{(Z')_2}{P=O}, \quad \underset{Z'}{C=O}, \text{ or } C\equiv$$

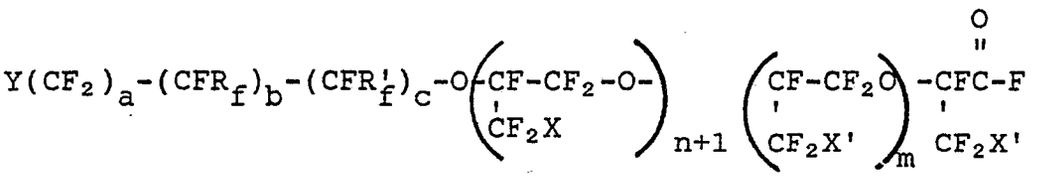
where Z' is F, Cl, Br, OH, NRR' or OA;

R and R' are independently selected from the group consisting of hydrogen, an alkyl having one or more than one carbon atom and an aryl,

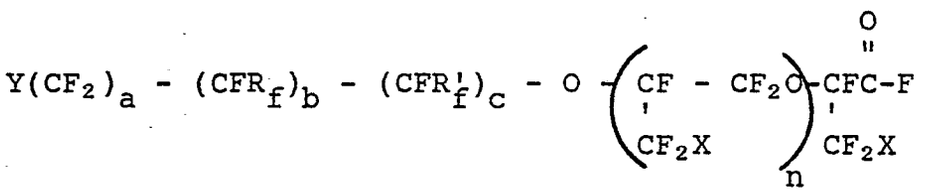
A is an alkali metal, quaternary nitrogen or R.

10. The method of Claim 7, 8 or 9 wherein n = 0 or 1 and X' = Cl.

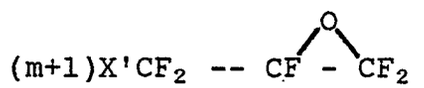
11. A method for preparing compounds of the formula



which comprises reacting compounds of the formula



with compounds of the formula



for a time and a temperature sufficient to form said compound;

wherein

a = 0 or an integer greater than 0;

b = 0 or an integer greater than 0;

c = 0 or 1 provided a + b + c ≠ 0;

m = zero or an integer greater than zero;

n = zero or an integer greater than zero;

R_f and R'_f are each independently selected from the group consisting of F, Cl, perfluoroalkyl and fluorochloroalkyl;

X' is independently Cl or Br;
X = F, Cl, Br, or mixtures thereof when n $\geq$ 1;
Y is an acid group or an acid derivative easily convertible to an acid group.

12. The method of Claim 11 wherein a = 0 - 3, b = 0-3, n = 0-6 and m = 0-6.

13. The method of Claim 11 or 12 where Y is selected from the group consisting of

$$Z'SO_2, \quad \begin{matrix} P{=}O, \\ (Z')_2 \end{matrix} \quad \begin{matrix} C{=}O, \\ Z' \end{matrix} \text{ or } C{\equiv}N$$

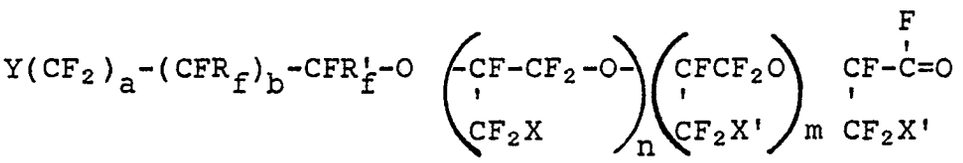
where Z' is F, Cl, Br, OH, NRR' or OA;
R and R' are independently selected from the group consisting of hydrogen, an alkyl having one or more than one carbon atom and an aryl,
A is an alkali metal, quaternary nitrogen or R.

14. The method of Claim 11, 12 or 13 where X = F and X' = Cl.

15. A method for preparing compounds of the formula

$$Y(CF_2)_a\text{-}(CFR_f)_b\text{-}CFR'_f\text{-}O\text{-}\left(\begin{matrix} CF\text{-}CF_2\text{-}O \\ | \\ CF_2X \end{matrix}\right)_n\left(\begin{matrix} CFCF_2O \\ | \\ CF_2X' \end{matrix}\right)_m \begin{matrix} Z \\ | \\ CF\text{-}C = O \\ | \\ CF_2X' \end{matrix}$$

which comprises reacting compounds of the formula



with compounds of the formula PZ for a time and temperature sufficient to form said compound;

wherein a = 0 or an integer greater than 0;
b = 0 or an integer greater than 0;
m = zero or an integer greater than zero;
n = zero or an integer greater than zero;
R_f and R'_f are each independently selected from the group consisting of F, Cl, perfluoroalkyl and fluorochloroalkyl;
X = F, Cl, Br, or mixtures thereof when n>1;
X' is independently Cl or Br;
Y is an acid group or an acid derivative easily convertible to an acid group;
Z = OH, NRR' or OR;
R and R' are independently selected from the group consisting of hydrogen, or an alkyl having one or more than one carbon atom and aryl;
P is a cation or a group that forms a cation.

0041736

European Patent Office

EUROPEAN SEARCH REPORT

Application number EP 81 10 4466

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim
A,D	US - A - 3 282 875 (D.J. CONNOLLY et al.) * Claims 1,7 *	1
A	US - A - 3 351 619 (J.L. WARNELL) * Column 1, lines 41-50 *	1
A	FR - A - 1 422 147 (E.I. DU PONT DE NEMOURS) * Résumé 6 *	1
A	FR - A - 1 341 087 (E.I. DU PONT DE NEMOURS) * Page 1 *	1

CLASSIFICATION OF THE APPLICATION (Int. Cl.³)

C 07 C 143/70
67/343
69/708
C 07 F 9/40

TECHNICAL FIELDS SEARCHED (Int. Cl.³)

C 07 C 143/70
67/343
69/708
C 07 F 9/40

CATEGORY OF CITED DOCUMENTS

X: particularly relevant
A: technological background
O: non-written disclosure
P: intermediate document
T: theory or principle underlying the invention
E: conflicting application
D: document cited in the application
L: citation for other reasons

&: member of the same patent family, corresponding document

X The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	01-09-1981	SAGATYS